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MANOSECOND LASER PHOTOLYSIS OF OPAQUE HETEROGENEOUS  
PHOTOSENSITIZERS(U) LOUGHBOROUGH UNIV OF TECHNOLOGY  
(ENGLAND) F WILKINSON OCT 87 DAJA45-85-C-0010

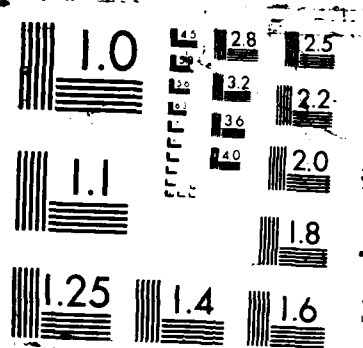
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Title of Research Project

NANOSECOND LASER PHOTOLYSIS OF OPAQUE  
HETEROGENEOUS PHOTSENSITIZERS

Name of Principal Investigator

F. Wilkinson

Name of Contractor

H. Brooks

Contract Number

DAJA 45-85-C-0010

*Loughborough Univ of Technology,  
England*

SIXTH PERIODIC REPORT

May 1987 - October 1987

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PART 1 ✓

(1) Work continues on studies of photophysical and photochemical properties of benzoylated polystyrene (polymer-bound benzophenone). We are able to establish the presence of two transients when these samples are subjected to laser flash photolysis exciting at 354 nm from the time dependent decrease in diffuse reflectance at different analysing wavelengths. One of these transients is the triplet state of the polymer bound benzophenone which can also be studied in emission which we have been able to do. The other is probably the radical formed by hydrogen abstraction by this triplet state by those photo excited species which are close enough to methylene groups to allow reaction.

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Attempts are being made to improve the signal to noise ratio on this data to enable a separation of the broad overlapping transient spectra and in order to determine the complex decay modes of both of these transients. This work is being carried out in collaboration with Professor J. Font and Dr J.L. Bourdelande from The Universitat Autònoma de Barcelona, in Spain. Dr Willsher spent two weeks in Spain during the Summer working on this project and presented a poster at the XIIth Reunion Bienal de Química Orgánica de la Real Sociedad Española de Química, Córdoba, Spain, 23-25 September, entitled "Fase Sólida : Contribución de la "Laser Flash Photolysis" a la Elucidación de Mecanismos en Reacciones Fotoquímicas". Dr Willsher also attended the XIIIth International Conference on Photochemistry, Budapest, 2-7 August and orally presented a paper entitled "Photochemical and Photophysical Processes in Benzoylated Polystyrene".

(2) We continue to study electronic energy transfer at interfaces for example triplet energy transfer from benzyophenone to 1 methyl naphthalene has been studied on various surfaces including silica gel, micro-crystalline cellulose, TiO<sub>2</sub> etc. Energy transfer on microcrystalline cellulose has been shown to be a static quenching mechanism in contrast to the situation in homogeneous solution where dynamic diffusion controlled energy transfer occurs. Other surfaces give more or less contributions via a dynamic mechanism.

Professor Wilkinson attended the 1987 'Internation Conference on Luminescence in Beijing, China where he chaired one of the sessions and presented a paper to appear in the Journal of Luminescence entitled 'Diffuse Reflectance Laser Flash Photolysis Studies of Energy Transfer at Interfaces'. He also attended by invitation the NATO Advanced Research Workshop on 'Photoinduced Charge Separation and Energy Migration in Supramolecule Species'. At this workshop he presented a paper entitled 'Competitive Energy and Electron Transfer Quenching of the Triplet States of Organic Compounds by Cr(tfac)<sub>3</sub> and Cr(tfbzac)<sub>3</sub> in Benzene'. In addition to taking a full part in the discussion at this meeting Professor Wilkinson acted as joint Chairman at one of the scientific discussions.

(3) The work on the behaviour of Ru<sup>2+</sup> complexes in functionalised polymers and held in cationic exchanges continues to yield interesting results. A number of studies have been made as a function of laser intensity and also as a function of loading on the ion exchange resin. Four complexes have been used which are Ru(bpy)<sup>2+</sup><sub>3</sub>, Ru(bpy)<sub>2</sub>(TAP)<sup>2+</sup>, Ru(bpy)(TAP)<sub>2</sub><sup>2+</sup> and Ru(TAP)<sub>3</sub><sup>2+</sup>, where bpy represents bipyridyl and TAP represents (1,4,5,8-tetra-

azaphananthrene. The kinetic behaviour changes systematically and is reproducible. The decays however are complex and mechanisms to explain these are now being considered.

(4) Development of the second laser flash photolysis system for studying diffuse reflectance laser flash photolysis is continuing. The computer control of the various functions of this system have been installed and software to make the use of this equipment convenient is being developed by Dr Kelly within Professor Wilkinsons research group.

## PART 2

### Future Work

During the course of this contract many results have been obtained on a variety of systems. Our plans for the last six months are to work through these systematically preparing publications on as many as possible and carrying out any further crucial experiments which fill in gaps in our knowledge or pertain to specific problems which our research has already revealed. In this way we expect to be able to report that several papers have been published, accepted, and submitted during the final six months.

## PART 3

None

PART 4

None

PART 5

(a)	Total amount for 1st year:	\$ 29,490.00
	Interim Reports 1-3 Claim:	\$ 29,490.00
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	Amount unused after 1st year:	\$ NIL
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	Total amount for 2nd year:	\$ 32,140.00
	Claim for 2nd year:	\$ 32,140.00
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	Amount unused	\$ NIL
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	Total amount for 3rd year:	\$ 37,400.00
	Claim for last 6 months:	\$ 18,700.00
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	Amount unused	\$ 18,700.00
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(b) List of important property acquired with contract funds during this period - NONE.

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